THE COPOLYMERIZATION OF α,β-UNSATURATED CARBONYL COMPOUNDS AND RELATED TYPES

BY

GEORGE HOWARD McCAIN

A.B., Franklin College, 1949
M.S., University of Illinois, 1950

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THE COPOLYMERIZATION OF α,β-UNSATURATED CARBONYL COMPOUNDS AND RELATED TYPES

Introduction

Recent work in this Laboratory (1,2) and elsewhere (3) has shown that α,β-unsaturated ketones not containing a vinyl or vinylidene group of the type $CH_2 = C <$, hitherto considered incapable of homopolymerization or copolymerization, can undergo copolymerization with several monomers.

The purpose of the work reported in this thesis was to enlarge the scope of this discovery by extending it to the formation of heteropolymers involving other classes of α,β-unsaturated carbonyl compounds and related structures with ordinary vinyl monomers. This work was more specifically directed toward the goals:

I. To determine which α,β-unsaturated carbonyl compounds (not containing a vinyl or vinylidene group of the type $CH_2 = C <$) and related types would copolymerize with butadiene.

II. To determine what monomers, other than butadiene, would form copolymers with these compounds.

III. To determine the amount of these compounds incorporated in the copolymers formed with butadiene.

With the exception of the work mentioned above, the copolymerization of α,β-unsaturated carbonyl compounds and related types has not been studied from an academic viewpoint and most of the polymerizations involving these compounds which are reported, are found in the patent literature.

Discussion Of Results

The homopolymerization and copolymerization of α,β-

unsaturated carbonyl compounds and related structures, in which the double bond is also conjugated with an aromatic ring, has been studied. The compounds studied include methyl and ethyl cinnamate, cinnamic acid, cinnamonitrile, their furyl analogs, and cinnamaldehyde.

Cinnamaldehyde did not homopolymerize, but it did copolymerize with acrylonitrile, methyl vinyl ketone, isoprene and butadiene. It failed to copolymerize with vinyl acetate and with methyl methacrylate. Evaluation of the compounded butadiene-cinnamaldehyde copolymers showed that their low temperature properties, hysteresis values and oil resistance are all good, but that their tensile strengths are poor.

Cinnamic acid did not homopolymerize, but it copolymerized with methyl vinyl ketone, styrene and butadiene. Some slight evidence of copolymerization with methyl methacrylate was observed. The evaluation of the compounded cinnamic acid-butadiene copolymer has established that it possesses outstanding tensile strength and low temperature properties, poor oil resistance, and hysteresis values about equal to those of GR-S.

trans-Cinnamonitrile failed to homopolymerize, but it copolymerized with methyl methacrylate, styrene, isoprene and butadiene. No copolymer was obtained with vinyl acetate or with acrylonitrile. Evaluation of the compounded butadiene-cinnamonitrile copolymer showed poor oil resistance, fair tensile strength and good low temperature properties.

Ethyl cinnamate formed a homopolymer with an average molecular weight of about 7600 under conventional bulk polymerization conditions. This ester also copolymerized with butadiene; a physical evaluation of the compounded copolymer showed excellent low temperature properties and good stress-strain values, but poor oil resistance and inferior hysteresis properties.

Methyl cinnamate also formed a homopolymer whose average molecular weight was about 2380. Methyl cinnamate

copolymerized with methyl vinyl ketone, acrylonitrile, methyl methacrylate, styrene, isoprene and butadiene. Evaluation of the compounded butadiene-methyl cinnamate copolymer showed properties much like those of ethyl cinnamate, except that its hysteresis values were better.

Ethyl α-cyano-β-phenylacrylate copolymerized with methyl methacrylate, styrene and butadiene. Methyl α-cyano-β-phenylacrylate copolymerized with methyl vinyl ketone and with butadiene, but failed to form a copolymer with vinyl acetate.

Other compounds found to copolymerize with butadiene were α-cyano-β-phenylacrylic acid, β-(α-furyl)-acrylic acid, ethyl β-(α-furyl)-acrylate and β-(α-furyl)-acrylonitrile. α-Cyano-β-(α-furyl)-acrylic acid and its ethyl ester failed to form copolymers with butadiene.

A method of analysis using infrared absorption spectra was developed and applied to the determination of ester or aldehyde content of the copolymers of butadiene with cinnamaldehyde, cinnamic acid, methyl cinnamate and ethyl cinnamate.

The amounts of cinnamaldehyde, cinnamic acid, cinnamonitrile and methyl or ethyl cinnamate incorporated in their copolymers with butadiene indicated, in general, that the copolymerization reaction was considerably slower than the homopolymerization of butadiene.

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VITA

The author was born on November 15, 1924 in Flora, Indiana. He attended the public schools in Delphi, Indiana and graduated from Delphi High School in 1942. In September of 1942 he entered Franklin College. In May of 1943 he entered the Army of the United States and served in the European Theater. He was discharged in January of 1946 and reentered Franklin College in September of 1946. He received the degree Bachelor of Arts, *cum laude,* from that institution in June of 1949. He entered the Graduate College of the University of Illinois in September of 1949, receiving the degree Master of Science in 1950. He held a research assistantship from September of 1950 to February of 1953.